

# **Time- and Irradiance-Dependent Behavior of the Quantum Yield of Chlorophyll *a* Fluorescence**

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Award Number: N00014-00-1-0319  
<http://www.ocean.washington.edu/>

## **LONG-TERM GOALS**

The long-term goals for this project are to improve the capability for determining phytoplankton biomass in the ocean from hyperspectral, remotely-sensed chlorophyll *a* fluorescence and to better understand the variability associated with chlorophyll *a* fluorescence.

## **OBJECTIVES**

Fluorescence-based approaches for determining phytoplankton biomass have been under-utilized in comparison to applications based on blue/green wavelength reflectance ratios. In part, the under utilization is due to attenuation of the fluorescence signal by high water absorption in the red, in contrast to the greater transmission, and hence, depth penetration, of blue and green wavelengths. In near-shore mesotrophic and eutrophic environments with moderate to high concentrations of phytoplankton, the difference in absorption coefficients among all visible wavelengths diminishes, resulting in more spectrally flat reflectance spectra. At these high phytoplankton concentrations, the natural (or solar-stimulated) chlorophyll fluorescence signal increases. The net effect is that chlorophyll *a* fluorescence becomes a significant feature of the reflectance spectra in these waters.

The first objective of this study was to determine – in high biomass waters – the contribution of solar backscattering to reflectance at the wavelengths associated with chlorophyll *a* fluorescence. This determination was a prerequisite to our second objective, i.e., the determination of the behavior of chlorophyll fluorescence quantum yield in response to changing irradiance.

## **APPROACH**

One approach for removing solar backscattering from the water-leaving radiance spectrum utilizes linear interpolation of the reflectance spectrum between wavelengths bracketing the fluorescence emission spectrum (e.g. Culver and Perry 1997, Abbott and Letelier 1997), based on the assumption that reflectance due to solar backscattering is linear between 665nm and 750nm. In spectral bands where strong absorption features, such as the Q band of chlorophyll *a*, are present, this approach may not best represent the true spectral behavior of solar reflectance. In near-shore waters containing high phytoplankton biomass, the strong contribution of chlorophyll absorption in the red may influence the spectral behavior of solar backscattering. Measured absorption coefficients, backscattering

Report Documentation Page			Form Approved OMB No. 0704-0188		
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1. REPORT DATE <b>30 SEP 2002</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2002 to 00-00-2002</b>	
4. TITLE AND SUBTITLE <b>Time- and Irradiance-Dependent Behavior of the Quantum Yield of Chlorophyll a Fluorescence</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>University of Washington,School of Oceanography,,MS 35-7940,,Seattle,,WA, 98195</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <b>The long-term goals for this project are to improve the capability for determining phytoplankton biomass in the ocean from hyperspectral, remotely-sensed chlorophyll a fluorescence and to better understand the variability associated with chlorophyll a fluorescence.</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>5</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

coefficients, and spectral reflectance ratios were combined with a forward model of reflectance to estimate the spectral behavior of solar backscattering in the spectral region corresponding to chlorophyll fluorescence emission.

## WORK COMPLETED

Absorption was measured with a WET Labs ac-9, backscattering with a HOBI Labs Hydroscat-6, spectral upwelling radiance and downwelling irradiance with a Biospherical Instruments PRR-800/810, and temperature and salinity were measured with a SeaBird CTD at a number of optically-diverse stations within Puget Sound, Washington. Absorption coefficients of particles plus chromophoric dissolved organic matter (CDOM) were determined by first removing the contribution of “pure” water (operationally defined as the signal obtained with Barnstead NANOpure Infinity water); secondly, by correcting for salinity and temperature effects at 715 nm; and thirdly, by applying a spectral scattering correction based on the magnitude of the  $a(715)$  signal and the spectral structure of backscattering as determined from the Hydroscat-6. The backscattering coefficients were determined according to Maffione and Dana (1997) and spectral structure of backscattering interpolated for other wavelengths in the spectral region between 415 and 715 nm.

Because the spectral structure of solar backscatter in the absence of chlorophyll fluorescence cannot be measured in the spectral region influenced by fluorescence, fluorescence-free reflectance must be modeled. The HYDROLIGHT (Mobley, 1994) radiative transfer model was used with measured absorption and backscattering coefficients as inputs. However, closure-type evaluations were first performed to determine whether the measurement coefficients were of sufficient quality.

Analysis of time series of fluorescence and quantum yields of fluorescence, based on corrections for solar backscattering, are continuing and should be completed during the coming year.

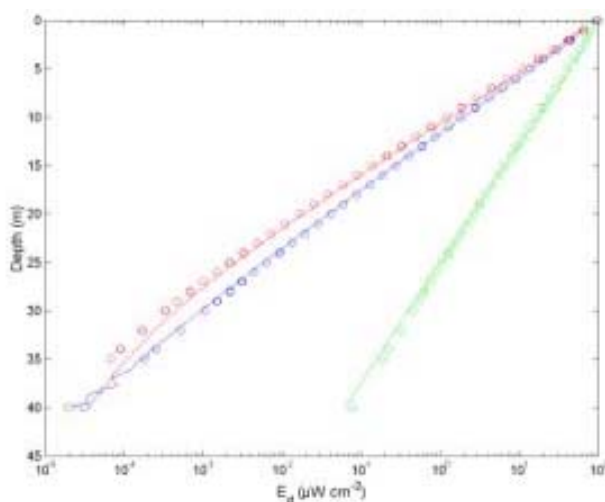
## RESULTS

Figure 1. Downwelling irradiance profiles ( $E_d$ ) at blue, green, and red wavelengths were modeled with HYDROLIGHT using measured absorption and backscattering coefficients as input (modeled values are indicated as open circles). The modeled values for  $E_d$  compared very well with values directly measured with the PRR-800 (measured values are indicated by solid lines). These quasi-closure results indicate that the measured absorption and backscattering coefficients are of sufficient quality to use in modeling fluorescence-free reflectance spectra.

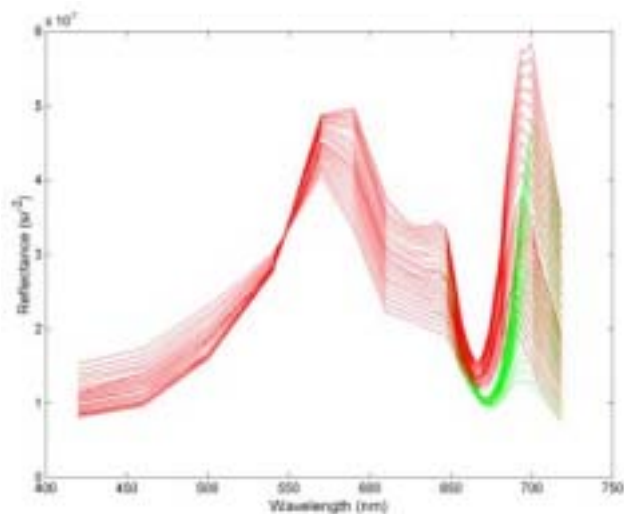
The results of modeling solar reflectance without a fluorescence terms indicate that there is very little spectral structure in solar backscattering (in the absence of fluorescence) under low chlorophyll conditions, i.e. the spectrally flat correction is appropriate. However, under increasing chlorophyll concentrations, the spectral structure of the solar backscattering reflectance increases significantly, due to anomalous dispersion. At high chlorophyll concentrations, the model predicts that chlorophyll fluorescence itself will have a reduced impact on the shape of the reflectance spectrum, but rather will be significantly constrained by solar backscattering.

Figure 2 shows the reflectance in the absence of fluorescence (green lines). As chlorophyll concentrations increase, the peak of the solar reflectance spectra shifts to the red. The net result is that the combined spectra of solar reflectance and fluorescence (red lines) shifts from 683 nm to 700 nm. This shift is due primarily to backscattering in the presence of a strong absorption band, and is

not due to phytoplankton absorption of fluorescent photons with subsequent re-emission at longer wavelengths.



**Figure 1** (see text for explanation)



**Figure 2** (see text for explanation)

## IMPACT/APPLICATIONS

Understanding of the behavior of solar backscattering at concentrations of phytoplankton biomass typical of mesotrophic and eutrophic near-shore waters is important for using chlorophyll fluorescence as a diagnostic of phytoplankton biomass.

## RELATED PROJECTS

This project is coordinated with N00014-00-1-0211 under the direction of Dr. Mary Jane Perry at the University of Maine.

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